XVII.

THEORY OF ABSORPTION-BANDS IN THE SPECTRUM, AND ITS BEARING IN PHOTOGRAPHY AND CHEMISTRY.

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In order to present this communication clearly, I must apologize for reminding you of certain facts, which probably are familiar to you as well as to myself; and these may be summarized in the following review. The rays of light absorbed by a colored solution cannot always be determined by its apparent color; for instance, an aniline alkali blue salt of commerce will extinguish or neutralize green and yellow rays (between *b* and *D* lines in the solar spectrum), eosin (fluorescein) of commerce absorbs only the green rays, its greatest intensity being at the *E* lines, it should also be observed that this latter substance by transmitted light appears red, and by reflected light fluorescent green.

By the term "absorption" it is ordinarily meant that a colored solution by transmitted light allows only those light rays to pass which do not belong to itself: in other words, certain of these rays are extinguished or neutralized, whilst others are transmitted. To determine correctly which of these rays are absorbed and which are transmitted, we must examine, by means of a glass or other transparent prism, the sunlight (or other incandescent light) transmitted through the colored solution.

The explanation of absorption is usually given somewhat in the following manner: —

A colored solution owes its absorption-bands, seen in the spectrum from its transmitted sunlight, to the fact that the ether molecules are excited by the sunlight, or other source of illumination, to move in undulatory vibrations; and that certain of these waves are of the same length with those of the solution, and hence are extinguished or withheld, whilst all others of unequal length are allowed to pass through. This explanation is founded upon the analogy offered by the solar or Frauenhofer lines, which appear black because their monochromatic

rays pass through the gaseous vapor of the same substances placed between our eyes and the point of their combustion; and thus the original monochromatic rays are absorbed by this gaseous vapor.

The theory of absorption of colored solutions may also be explained, by assuming that certain of the rays excited in the solution are the result of the motion of waves of unequal length. Now, if we call to mind that each ray gives its own illumination or image of the slit, and consequently that there are side by side a series of these images, whose illumination is the result of the ether molecules vibrating in wave-lengths gradually increasing in length, — for instance, at the solar line *H′* being 3,928 according to Ångstrom's map, or $\frac{174}{10,000,000}$ in. to 7605 or $\frac{266}{10,000,000}$ in. at *A* line, — we may easily conceive that certain of these ether molecules, passing through a solution whose molecules are of a size capable of receiving their motion, transfer their energy; whilst certain others of different length, both of longer and shorter size, only partially transfer their energy; and again certain others, not losing any of their energy, because they do not excite any motion of their own kind, pass through at the same initial rate. The consequence would follow, that the first set of waves become extinguished, and hence their illumination ceases, after their projection into the solution; the second rays are partially quenched; and the third set appear as bright as when first projected. Thus, instead of seeing the absorption-bands of the spectrum transmitted through a colored solution, always with definite limits, in some instances we observe that the greatest amount of light absorbed is at the middle, and shades lighter towards the outside limits of these bands. The energy consumed in extinguishing certain rays of light must, then, by the law of conservation of energy, become stored up in a latent form in all those colored substances which give absorption-bands.

Herrmann Vogel (Jahresbericht, 1861, and in Watt's Dict. of Chem. vol. v. p. 295) maintained that silver iodide or bromide or chloride are reduced by certain rays of solar light to the subiodide, subbromide, and subchloride; or, in other words, —

$$2\ (Ag.\ Br.),$$

by exposure to those refrangible rays of light which to our eye appear violet or blue, becomes

$$Ag.^2\ Br.,$$

and that one portion of bromine is set free.

A year or two ago, Vogel, as has already been referred to by me, in a previous communication to this Academy, observed that the addition of certain pigments, chiefly aniline, to the above-named silver bromide salt, would cause a partial reduction of the silver salt, when these were exposed to rays of less refrangibility than the blue. He explained this phenomenon by supposing that the pigment corallin or fuchsin, which has a red color, absorbed and stored up latent energy, and so re-enforced the primary action on the silver bromide. Captain Abney, as has also been stated, informed me last year that the addition of gum benzoin increased likewise the sensitive action on the silver bromide, so that by its addition he could photograph the less refrangible rays of the solar spectrum. He has publicly, in his South Kensington address, explained this increased action on the principle that the molecules of silver bromide rotating and vibrating at a given rate were weighted down and moved at a slower rate, so that the interference of rays of less refrangibility than what constitutes blue light would reduce the strained bromide silver salt, and so give an image from green and yellow light. This he explained on the principle that these silver bromide molecules consequently could be made to swing in discord with waves of greater amplitude.

If Vogel's explanation is correct, we should suppose that any pigment which absorbs the green or yellow rays, and does not prevent the chemical process of reduction, would likewise increase the sensitiveness of the silver salt to these rays. Now, the same aniline blue that I mentioned at the beginning of this communication absorbs green and yellow rays, and does not prevent the reduction of silver bromide to rays of blue light. This blue-stained silver bromide was exposed to the solar spectrum from about line *G* to line *A*, and yet I could obtain no image below line *F* in the blue. Again, if a silver bromide emulsion (so called) be stained with the same aniline colors which Vogel himself used, — viz., fuchsin or corallin, — we ought to have the silver salt reduced on exposure to the green rays of light. Unless there be free nitrate of silver in the emulsion, we get no such effect. These two experiments conflict with Vogel's explanation. Captain Abney states that, if there is an excess of silver bromide, the addition of the aniline does not increase its sensitiveness to the less refrangible rays. Now, if there is an excess of silver bromide, there can be no free silver nitrate; and, unless there be free nitrate, there is no action from the pigment and silver bromide. The explanation of this photographical action of the green and yellow rays of light must be sought out in some other way.

If an aqueous solution of eosin (fluorescein, a rather complicated organic compound) be added to a neutral solution of silver nitrate, a colored precipitate is thrown down. It seems to me that the precipitate obtained from the addition of silver nitrate to the eosin is a definite salt of silver; and this is shown in the following way: Wash the precipitate of eosin and silver nitrate with distilled water, until all trace of an excess of silver nitrate is removed; then dissolve this washed precipitate in a strong solution of sodium hyposulphite, until the latter is saturated; then add to this saturated solution a solution of cadmium or potassium bromide. A precipitate is thrown down, which is again soluble in more of the sodium hyposulphite. Now, if this salt of silver eosin be precipitated upon a film which contains neither bromide, chloride, or iodide of silver, a definite picture of the green rays of the spectrum will be obtained. This image which I now exhibit corresponds to that part of the spectrum which this silver salt absorbs, as may be seen on comparing it with the absorption spectrum of an emulsion of this salt which has been prepared for that purpose.

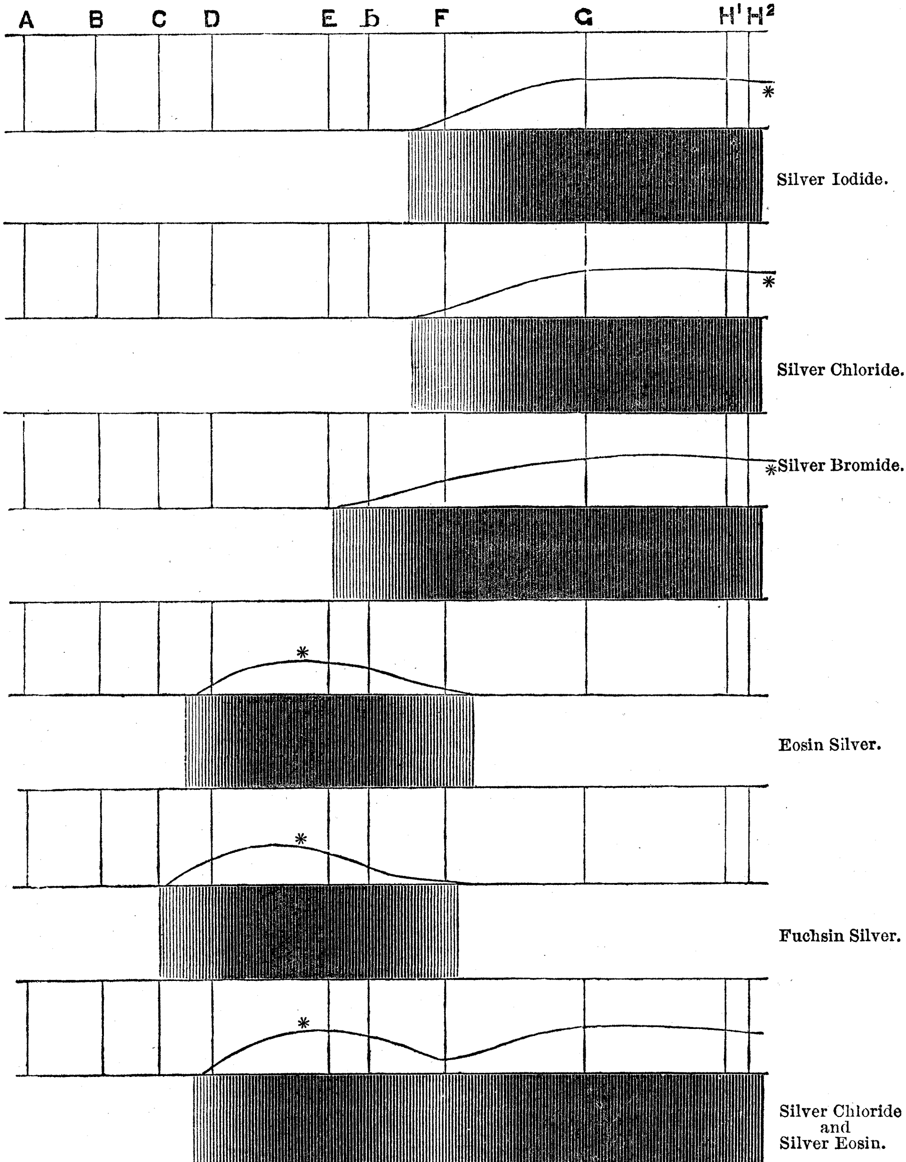
Commercial aniline chloride is a salt of which the coloring matter in solution absorbs violet, and also the green rays between F and D lines of the solar spectrum; its greatest intensity being at E line of the solar spectrum. Here is a definite image of those rays, which corresponds with absorption-bands of this silver salt. All three plates were exposed to the spectrum for about ten minutes only. We will go still further. Silver iodide absorbs the violet and the more refrangible blue rays. It is these rays only that reduce this silver salt. In other words, 2 (Ag. I.) is reduced to Ag^2 I., on its exposure to the rays of light which this salt absorbs. Argentic chloride, on exposure to those refrangible blue rays which it absorbs, becomes argentous chloride. Argentic bromide, on exposure to those refrangible blue rays (down to line F) which it absorbs, becomes argentous bromide. The intensity of photographical action corresponds to that of absorption. Neither of these salts are affected by rays of less refrangibility than those which they absorb; yet there may be slight action extending below the invisible band, corresponding with an extended and faint absorption below this point. I would therefore deduce a general proposition founded on these experiments, and expressed in the following terms: —

A colored silver salt is reduced by rays of light of the same refrangibility which it absorbs.

I would propose the following theory as being very probable: The

colored silver salt owes its cohesion to the fact that the combined salt. when exposed to light, has a molecular vibration, expressed in waves of definite length. The addition of rays of light which may be in discord or in accord with the vibration disturbs the cohesion, and hence either the whole or part of the combining acid is set free. The annexed diagram will serve to illustrate the relation between the absorption and photographical action of some of the silver salts.

By using a long focus collimating lens, practical experience shows that not only do we obtain more illumination of the spectrum, but that we can also bring into vision the ultra violet and red rays; so that the solar lines to L can be distinctly seen, as also the A lines.



* Lines showing curve of intensity of absorption and photographical action.